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## (54) COMPOSITION WITH ANTIMICROBIAL AND DEODORIZING PERFORMANCE

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain the subject composition excellent in mechanical strength, feel of touch and productivity, by immersing protein fibers in a metal ammine complex alkaline solution so as to carry a lot of metal thereon.
SOLUTION: This composition consisting of protein fibers carrying metal thereon and having antimicrobial and deodorizing performance is obtained by immersing protein fibers such as wool, silk and feather in a metal ammine complex alkaline solution such as copper ammine complex, zinc ammine complex or silver ammine complex. Preferably, the composition is formed into such a shape or pattern as that of cotton, thread, braid, woven fabric, paper sheet, nonwoven fabric, powder, microbeads, film, sponge, honeycomb, cylinder or block so as to produce a formed product.

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* NOTICES *



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CLAIMS

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[Claim(s)]
[Claim 1] The constituent which has antibacterial deodorization and the deodorization engine performance which protein fibers were made to support a metal by being immersed in a metal ammine complex solution in protein fibers.
[Claim 2] The constituent which has the antibacterial deodorization according to claim 1 and the deodorization engine performance which are at least one kind chosen from the group which a metal ammine complex becomes from a copper ammine complex, a zinc ammine complex, and a silver ammine complex.
[Claim 3] The manufacture approach of a constituent of having the antibacterial deodorization and the deodorization engine performance which consist of protein fibers which is characterized by being immersed in a metal ammine complex alkali solution in protein fibers, and which supported the metal.
[Claim 4] The manufacture approach according to claim 3 characterized by being the protein fibers to which pretreatment which protein fibers are immersed in an acid or an alkali water solution, and it rinses after that was performed.
[Claim 5] The manufacture approach according to claim 3 or 4 characterized by being at least one kind chosen from the group which a metal ammine complex becomes from a copper ammine complex, a zinc ammine complex, and a silver ammine complex.
[Claim 6] About a constituent according to claim 1 or 2, they are the shape of the shape of the shape of the shape of the shape of the shape of the shape of the shape of the shape of curdy and yarn, and a string, and textiles, and paper, a nonwoven fabric, powder, and a micro bead, and a film, and sponge, and a honeycomb, and the molding fabricated tubed or massive.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the constituent with which antibacterial deodorization nature and deodorization nature consist of good protein fibers. It is related with the constituent which has the antibacterial deodorization nature and deodorization nature which consist of protein fibers which supported the metal in detail.
[0002]
[Description of the Prior Art] Conventionally, there are much reports about the constituent which consists of protein fibers which supported the metal. For example, supporting and combining a metal phthalocyanine with protein fibers, such as wool, and obtaining deodorization nature fiber is indicated by JP,61-258078,A and JP,1-111067,A.
[0003] There is a report of JP,5-65191,B about the deodorization nature fiber which a metal ammine complex is made to act and is obtained on the other hand. It being immersed in a metal ammine complex solution in celluloses, carrying out the chemical bond of a metal and the cellulose to this official report, and obtaining a deodorization nature constituent is indicated.
[0004]
[Problem(s) to be Solved by the Invention] However, there is still no report which a metal ammine complex is made to act on protein fibers, and obtains a deodorization nature protein fiber constituent. Moreover, the metaled support force over protein fibers is weak, this approach has a problem in wash endurance, and since the support rate is still slower, productivity is bad [ an approach ], although the method of being immersed in the dispersion liquid of copper carbonate or copper hydroxide in protein fibers, and making protein fibers support a metal directly is also considered about the deodorization nature protein fiber constituent which consists of protein fibers which supported the metal directly. Moreover, in order to improve the metaled support force and metaled support rate to protein fibers in said approach, when pretreatment special to protein fibers etc. is performed, there are problems, such as spoiling the front face (aesthetic property) and physical characteristic (reinforcement) of protein fibers before pretreatment.
[0005] That is, this invention is excellent in the metaled support nature (the support force and support rate) to protein fibers, and makes it a technical problem to offer the constituent which has the antibacterial deodorization and deodorization nature which consist of protein fibers which supported directly the metal which does not spoil the front face (aesthetic property) or physical characteristic (reinforcement) of protein fibers before processing.
[0006]
[Means for Solving the Problem] This invention is as follows.
1. Constituent which has antibacterial deodorization and deodorization engine performance which protein fibers were made to support metal by being immersed in metal ammine complex solution in protein fibers.
2. Constituent which has antibacterial deodorization and deodorization engine performance of one above-mentioned publication which are at least one kind chosen from group which metal ammine complex becomes from copper ammine complex, zinc ammine complex, and silver ammine complex.
3. Manufacture approach of constituent of having antibacterial deodorization and deodorization engine performance which consist of protein fibers which is characterized by being immersed in metal ammine complex alkali solution in protein fibers, and which supported metal.
4. Manufacture approach of three above-mentioned publication characterized by being protein fibers to which pretreatment which protein fibers are immersed in acid or alkali water solution, and it rinses after that was performed.

5. Manufacture approach the above 3 characterized by being at least one kind chosen from group which metal ammine complex becomes from copper ammine complex, zinc ammine complex, and silver ammine complex, or given in four.
6. About a constituent the above 1 or given in two, they are the shape of the shape of the shape of the shape of the shape of the shape of the shape of the shape of curdy and yarn, and a string, and textiles, and paper, a nonwoven fabric, powder, and a micro bead, and a film, and sponge, and a honeycomb, and the moldings fabricated tubed or massive.
In addition, the antibacterial deodorization nature as used in the field of this invention points out the effectiveness of preventing the nasty smell generated from a coccus etc. by the antibacterial action in order to prevent the nasty smell generated from Staphylococcus aureus etc., and deodorization nature points out the deodorization effectiveness over malodorous substances, such as a hydrogen sulfide, ammonia, various amines, various mercaptans, and formalin.
[0007] The constituent of this invention does the following effectiveness so.
** The metaled support force over protein fibers is strong. It excels in wash endurance.
** Don't spoil the front face (aesthetic property) or physical characteristic (reinforcement) of protein fibers before processing.
** Excel in the deodorization nature to a malodorous substance.
** Excel in the nasty smell prevention generated from a coccus etc. by the antibacterial action which a metal atom has.
** There is no performance degradation by wash.
[0008] Moreover, the manufacture approach of the constituent of this invention does the following effectiveness so.
** Protein fibers can be made to support a lot of metals.
** A metal supports very quickly to protein fibers.
** A metal ammine complex and the dirt by omission of metaled powder are not generated among a production process.
** It can produce continuously.
** ** - ** are excelled in productivity.
[0009] Moreover, the moldings which fabricated the constituent of this invention does the following effectiveness so.
** Since a metal ammine complex and the dirt by omission of metaled powder are not generated, there is very little contamination by powder adhesion in mold goods.
[0010] Hereafter, this invention is explained to a detail. If the compound containing basic nitrogen, such as ammonia or an amine, an imine, and an imidazole, is added to electrolytic solutions, such as the sulfate of metals, such as copper, zinc, and silver, a chloride, a nitrate, phosphate, acetate, and a hydroxide, a metal ammine complex will generate. Generally the metal complex has configurated one or more sorts of ligands. It is the same, and the ammine complex also made the ligand the compound containing basic nitrogen, such as ammonia or an amine, an imine, and an imidazole, and has configurated it one or more sorts. There is the number of the respectively most stable ligands according to a metaled class, for example, four ligands are stable when it is a copper complex. Although a chemical bond can be carried out to protein fibers with any coordination numbers, if the compound containing the aforementioned basic nitrogen more than a mole ratio which becomes a metal and the most stable form is added, a good metal ammine complex solution will be obtained. In alkalinity, this complex is stable, melts in water well, and gives a uniform metal ammine complex ion solution.
[0011] Although it is good without limit if the concentration of the aforementioned electrolyte is below solubility, and the scale factor to the electrolyte of the compound containing basic nitrogen is also good without limit, the water solution which contains a mol for the compound which contains basic nitrogen 0.5 to 30% of the weight by using the electrolyte concerned as a metal atom preferably four to 12 times to the electrolyte concerned is suitable. The amount of the metal ammine complex which will not be combined if there are few metal atoms concerned than 0.5 % of the weight, and a support rate will be slow and will increase more than 30 % of the weight also increases, and a loss increases in the case of washing after processing. Since all the electrolytes concerned do not become an ammine complex but precipitate as a hydroxide in part when the scale factor to the electrolyte concerned of the compound containing basic nitrogen is lower than the scale factor most formed in stability, sufficient support rate and the support force are not acquired about what precipitated.
[0012] In this way, if immersed in the obtained metal ammine complex solution in protein fibers, such as

wool yarn, such as the shape of fibrous and a film, and massive, a silk, and feathers, metal ammine complex ion and protein fibers will react very quickly, and the constituent which has the antibacterial deodorization and the deodorization engine performance in which metal ammine complex ion and protein fibers carried out the chemical bond is given. This support is very quick and a cause deer also supports a metal firmly. The immersion time amount for about 30 seconds is enough practical. If a superfluous metal ammine complex is removed by deliquoring and rinsing this, the constituent which consists of protein fibers which supported the metal firmly will be obtained. The metal with which after rinsing is supported is carrying out the firm chemical bond to protein fibers.

[0013] Copper, zinc, and silver are mentioned as a metal which protein fibers are made to support.

[0014] As protein fibers used in this invention, ingredients containing these, such as wool yarn, a silk, and feathers, are mentioned. Moreover, although the shape of fibrous and a film (the shape of the shape of textile fabrics and a nonwoven fabric), massive, etc. are mentioned as a configuration, the thing of the configuration which can be produced continuously is desirable.

[0015] The constituent of this invention can be obtained by being immersed in a metal ammine complex alkali solution in protein fibers as above-mentioned. By using this metal ammine complex alkali solution, protein fibers can be made to support a lot of metals very quickly, and the metal ammine complex from the supported protein fibers and the dirt by omission of metaled powder are not generated from the support force of the metal of protein fibers being still stronger. Furthermore it can produce continuously, and since the production rate is very quick, it excels in productivity.

[0016] Moreover, compared with what does not pretreat, a constituent with the strong support force with a quick and support rate can also be obtained by performing pretreatment immersed in an acid or an alkali water solution in the protein fibers (the protein fibers before processing) before being immersed in a metal ammine complex alkali solution. This is to hydrolyze proteinic peptide linkage partially and for the amino group and a carboxyl group to arise, if protein is contacted in an acid or an alkali water solution, and since the chemical bond of the amino group and a carboxyl group, and the metal ammine complex ion is carried out easily, its metaled support rate and metaled support force of protein fibers also improve. However, in order to raise a support rate and the support force, since the inclination for the front face (aesthetic property) and physical characteristic (reinforcement) of the protein fibers themselves to fall is shown when peptide linkage is made to hydrolyze, using in the next range is desirable [ the amino group and a carboxyl group are produced, that is, / the processing liquid used for pretreatment ]. (1) It is [ 50 or less % of the weight of concentration ] the alkali water solution of 1 - 20 % of the weight of concentration preferably the acid water solution of 1 - 20 % of the weight of concentration, or 50 or less % of the weight of (2) concentration.

[0017] Together with the material of independent or others, the shape of the shape of the shape of the shape of the shape of the shape of the shape of the shape of curdy and yarn and a string and textiles and paper, a nonwoven fabric, powder, and a micro bead and a film and sponge and a honeycomb, tubed, massive, etc. can carry out processing shaping of the constituent of this invention obtained as mentioned above at all forms. Moreover, since the constituent of this invention itself has very little contamination by powder and there is still very less contamination by powder also in the time of processing, contamination by powder adhesion in mold goods has very few advantages.

[0018]

[Example] Although an example is raised to below and this invention is explained to it, this invention is not limited to these. In addition, each evaluation approach of the constituent of an example is based on below.

[0019] The schematic diagram of the equipment of a deodorization performance test deodorization performance test is shown in drawing 5 . 1. Attach the connector with a cock in the fastener bag of 5L capacity as degassing opening, gas-charging opening, and an indicator tube entry beforehand. 1g of test portions is paid to a fastener bag, and after shutting a fastener completely and deaerating it, 1.5L enclosure of a 100 ppm hydrogen sulfide is done using a pump. Enclosure end time is made into 0 minute, and gas concentration is measured with a Kitagawa style indicator tube for every fixed time amount progress. In addition, the hydrogen-sulfide chemical cylinder beforehand prepared by 100 ppm was used for the hydrogen sulfide in evaluation of this example.

[0020] Wash trial JIS L-0217 It applied to 103 law correspondingly.

[0021] It applied to the number-of-microorganism measuring method of "the working effect evaluation trial manual of an antibacterial deodorization processing product" which an antibacterial trial textiles sanitary finishing conference defines correspondingly. In addition, Staphylococcus aureus was used for the trial fungus body in evaluation of this example.

[0022] In the copper-sulfate water solution of 13 % of the weight of examples, the aqueous ammonia of

concentration was added 25% of the weight, and the copper ammine complex water solution of a navy blue color was obtained so that ammonia might become the 6 time mol of a copper sulfate. At the room temperature, it was immersed for 30 seconds, subsequently purification wool was rinsed [ deliquored it and ] and dried, and the wool (constituent 1) which supported copper was obtained so that a bath ratio might increase to this 30 times. The evaluation result of the obtained constituent 1 was as follows. The deodorization engine performance to a hydrogen sulfide is shown in drawing 1 . For a copper content, the content after 4.0 % of the weight of constituent 1 Naka and a wash trial (10 times) is 3.9 % of the weight. For an antibacterial test result, the antibacterial test result after 4.2 and a wash trial (10 times) is 4.0. Moreover, as compared with the purification wool which hits a raw material, the aesthetic property of the constituent 1 was comparable, and it showed the equivalent value as it also showed physical physical properties in Table 1.

[0023]

[Table 1]

| | 精製羊毛 | 組成物 1 |
|---|---|---|
| 乾強度 (g／d) | 1．4 | 1．4 |
| 湿潤強度 (g／d) | 1．2 | 1．2 |
| 伸度 ( % ) | 30 | 30 |

[0024]

[Drawing 1]

[0025] The aqueous ammonia of concentration was added to the water solution of the zinc sulfate of 23 % of the weight of examples 25% of the weight so that ammonia might become the 6 time mol of a zinc sulfate, and the transparent and colorless zinc ammine complex water solution was obtained. The feathers (constituent 2) which were immersed for 30 seconds, subsequently rinsed [ deliquored them and ] and dried the feathers for feather quilts at the room temperature, and supported zinc were obtained so that a bath ratio might increase to this 30 times. The evaluation result of the obtained constituent 2 was as follows. The deodorization engine performance to a hydrogen sulfide is shown in drawing 2 . A zinc content is 3.8 % of the weight of constituent 2 Naka, and an antibacterial test result is 3.7. From this result, it is admitted that a constituent 2 has sufficient antibacterial deodorization and the deodorization engine performance.

[0026]

[Drawing 2]

[0027] In the silver chloride water solution of 33 % of the weight of examples, the aqueous ammonia of concentration was added 25% of the weight, and the silver ammine complex water solution was obtained so that ammonia might become the 6 time mol of a silver chloride. The silk fabrics (constituent 3) which were immersed for 30 seconds, subsequently rinsed [ deliquored them and ] and dried silk fabrics at the room temperature, and supported silver were obtained so that a bath ratio might increase to this 30 times. The evaluation result of the obtained constituent 3 was as follows. The deodorization engine performance to a hydrogen sulfide is shown in drawing 3 . For a silver content, the content after 3.9 % of the weight of constituent 3 Naka and a wash trial (10 times) is 3.8 % of the weight. For an antibacterial test result, the antibacterial test result after 3.8 and a wash trial (10 times) is 3.6. From this result, it is admitted that a constituent 3 has sufficient antibacterial deodorization and the deodorization engine performance.

[0028]

[Drawing 3]

[0029] The activation wool (constituent 4) which supported copper like the example 1 was obtained except having used the pretreatment wool (activation wool) which was immersed for 10 minutes, deliquored, rinsed, subsequently dried, and obtained purification wool at the room temperature instead of the purification wool used for example 4 example 1 so that a bath ratio might increase in a sulfuric-acid water solution 30 times 5% of the weight. The evaluation result of the obtained constituent 4 was as follows. The deodorization engine performance to a hydrogen sulfide is shown in drawing 4 . For a copper content, the content after 4.8 % of the weight of constituent 1 Naka and a wash trial (10 times) is 4.7 % of the weight. For an antibacterial test result, the antibacterial test result after 4.7 and a wash trial (10 times) is 4.6. From this result, it is admitted that a constituent 4 has sufficient antibacterial deodorization and the deodorization

engine performance.
[0030]
[Drawing 4]
[0031]
[Effect of the Invention] This constituent can be made to support a lot of metallic compounds according to the manufacture approach of this invention, without spoiling properties, such as reinforcement of this constituent, and aesthetic property. since [ moreover, ] it can be made to support very quickly and the dirt by omission of metallic-compounds powder is generated neither at a production process nor a processing process -- productivity -- excelling . Moreover, it carries out in this way, and properties, such as reinforcement of constituent original [ constituent / which were obtained / the antibacterial deodorization and the deodorization nature constituent ], and aesthetic property, are not spoiled, but react with malodorous substances, such as sulfur compounds, such as alkylamines, such as ammonia and a trimethylamine, a hydrogen sulfide, and methyl mercaptans, and formalin, and the remarkable deodorization engine performance is demonstrated. On the other hand, the antibacterial action which a metal atom has shows antibacterial [ strong ] to Staphylococcus aureus etc. Moreover, since metallic compounds are firmly supported by the constituent, they are excellent in wash endurance etc.

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[Translation done.]

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DRAWINGS

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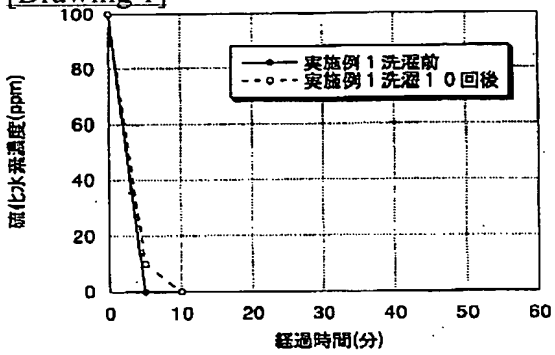
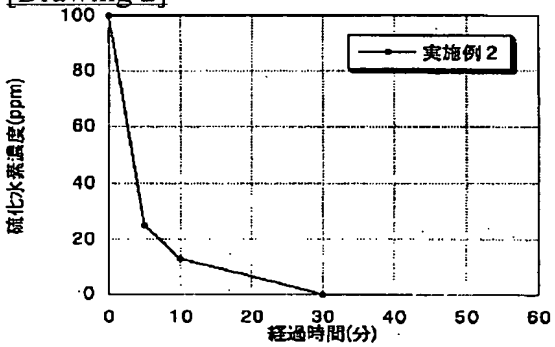
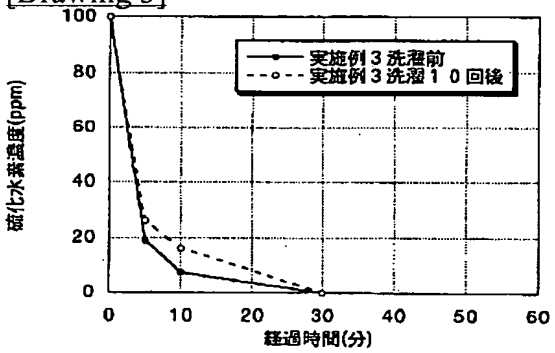
[Drawing 1]



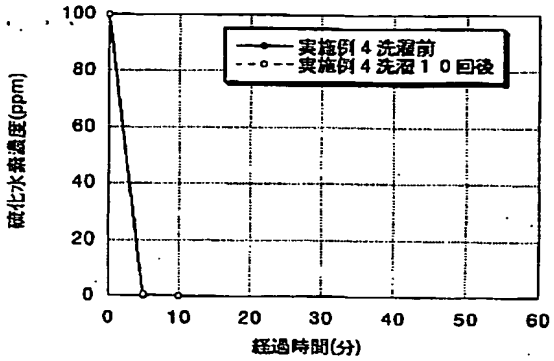

[Drawing 2]



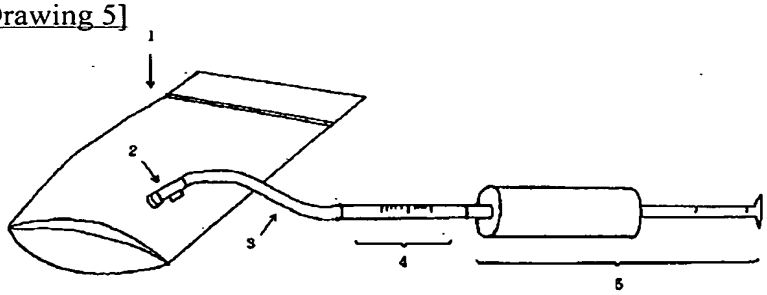

[Drawing 3]




[Drawing 4]




[Drawing 5]

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[Translation done.]

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審査請求　未請求　請求項の数６　ＦＤ　（全 5 頁）

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(54)【発明の名称】　抗菌防臭ならびに消臭性能を有する組成物

(57)【要約】
【課題】　蛋白質繊維類に対する金属の担持性（担持力及び担持速度）に優れ、処理前の蛋白質繊維類の表面（風合い）や物理的特性（強度）を損なうことがない、金属を直接担持した蛋白質繊維類からなる抗菌防臭性及び消臭性を有する組成物を提供する。
【解決手段】　金属アンミン錯体アルカリ溶液に蛋白質繊維類を浸漬して得る。

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【特許請求の範囲】

【請求項１】　金属アンミン錯体溶液に蛋白質繊維類を浸漬することにより、金属を蛋白質繊維類に担持させた、抗菌防臭ならびに消臭性能を有する組成物。

【請求項２】　金属アンミン錯体が、銅アンミン錯体、亜鉛アンミン錯体、銀アンミン錯体からなる群から選ばれた少なくとも１種類である請求項１記載の抗菌防臭ならびに消臭性能を有する組成物。

【請求項３】　金属アンミン錯体アルカリ溶液に蛋白質繊維類を浸漬することを特徴とする、金属を担持した蛋白質繊維類からなる抗菌防臭ならびに消臭性能を有する組成物の製造方法。

【請求項４】　蛋白質繊維類が、酸またはアルカリ水溶液に浸漬しその後水洗する前処理を施された蛋白質繊維類であることを特徴とする請求項３記載の製造方法。

【請求項５】　金属アンミン錯体が、銅アンミン錯体、亜鉛アンミン錯体、銀アンミン錯体からなる群から選ばれた少なくとも１種類であることを特徴とする請求項３又は４記載の製造方法。

【請求項６】　請求項１又は２記載の組成物を、綿状、糸状、紐状、織物状、紙状、不織布、粉末状、マイクロビーズ状、フィルム状、スポンジ状、ハニカム状、筒状又は塊状に成形した成型物。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は抗菌防臭性及び消臭性が良好な蛋白質繊維類からなる組成物に関する。詳しくは金属を担持した蛋白質繊維類からなる抗菌防臭性及び消臭性を有する組成物に関する。

【０００２】

【従来の技術】従来、金属を担持した蛋白質繊維類からなる組成物については数多くの報告がある。例えば、特開昭６１－２５８０７８号公報、特開平１－１１１０６７号公報等には、羊毛などの蛋白質繊維に、金属フタロシアニンを担持、結合させ消臭性繊維を得ることが開示されている。

【０００３】一方、金属アンミン錯体を作用させて得る消臭性繊維類について、特公平５－６５１９１号公報の報告がある。この公報には、金属アンミン錯体溶液にセルロース類を浸漬して金属とセルロースとを化学結合させ消臭性組成物を得ることが記載されている。

【０００４】

【発明が解決しようとする課題】しかし、金属アンミン錯体を蛋白質繊維類に作用させて消臭性蛋白質繊維類組成物を得る報告は未だない。また金属を直接担持した蛋白質繊維類からなる消臭性蛋白質繊維類組成物について、炭酸銅又は水酸化銅の分散液に蛋白質繊維類を浸漬して、蛋白質繊維類に金属を直接担持させる方法も考えられるが、この方法は蛋白質繊維類に対する金属の担持力が弱く洗濯耐久性に問題があり、さらに担持速度が遅

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いため生産性が悪い。また前記方法において蛋白質繊維類に対する金属の担持力や担持速度を改善するため蛋白質繊維類に特別な前処理等を行うと、前処理前の蛋白質繊維類の表面（風合い）や物理的特性（強度）を損なう等の問題がある。

【０００５】すなわち本発明は、蛋白質繊維類に対する金属の担持性（担持力及び担持速度）に優れ、処理前の蛋白質繊維類の表面（風合い）や物理的特性（強度）を損なうことがない、金属を直接担持した蛋白質繊維類からなる抗菌防臭ならびに消臭性を有する組成物を提供することを課題とする。

【０００６】

【課題を解決するための手段】本発明は、以下のとおりである。

１．　金属アンミン錯体溶液に蛋白質繊維類を浸漬することにより、金属を蛋白質繊維類に担持させた、抗菌防臭ならびに消臭性能を有する組成物。

２．　金属アンミン錯体が、銅アンミン錯体、亜鉛アンミン錯体、銀アンミン錯体からなる群から選ばれた少なくとも１種類である上記１記載の抗菌防臭ならびに消臭性能を有する組成物。

３．　金属アンミン錯体アルカリ溶液に蛋白質繊維類を浸漬することを特徴とする、金属を担持した蛋白質繊維類からなる抗菌防臭ならびに消臭性能を有する組成物の製造方法。

４．　蛋白質繊維類が、酸またはアルカリ水溶液に浸漬しその後水洗する前処理を施された蛋白質繊維類であることを特徴とする上記３記載の製造方法。

５．　金属アンミン錯体が、銅アンミン錯体、亜鉛アンミン錯体、銀アンミン錯体からなる群から選ばれた少なくとも１種類であることを特徴とする上記３又は４記載の製造方法。

６．　上記１又は２記載の組成物を、綿状、糸状、紐状、織物状、紙状、不織布、粉末状、マイクロビーズ状、フィルム状、スポンジ状、ハニカム状、筒状又は塊状に成形した成形物。

なお本発明でいう抗菌防臭性とは、黄色ブドウ状球菌等から発生する異臭を防止するため、抗菌作用によって球菌等から発生する異臭を防止する効果を指し、消臭性とは硫化水素、アンモニア、各種アミン、各種メルカプタン、ホルマリン等の悪臭物質に対する消臭効果を指す。

【０００７】本発明の組成物は、以下の効果を奏する。

①　蛋白質繊維類に対する金属の担持力が強い。洗濯耐久性に優れる。

②　処理前の蛋白質繊維類の表面（風合い）や物理的特性（強度）を損なうことがない。

③　悪臭物質に対する消臭性に優れる。

④　金属原子の持つ抗菌作用により、球菌等から発生する異臭防止に優れる。

⑤　洗濯による性能の低下がない。

【０００８】また、本発明の組成物の製造方法は、以下の効果を奏する。

① 蛋白質繊維類に大量の金属を担持させることができる。

② 金属が蛋白質繊維類に極めて速く担持する。

③ 製造工程中、金属アンミン錯体および金属の粉末の脱落による汚れが発生しない。

④ 連続生産が可能である。

⑤ ②～④より生産性に優れる。

【０００９】また、本発明の組成物を成形した成形物は、以下の効果を奏する。

① 金属アンミン錯体および金属の粉末の脱落による汚れが発生しないため、成形品への粉末付着による汚染が極めて少ない。

【００１０】以下、本発明を詳細に説明する。銅、亜鉛、銀等の金属の硫酸塩、塩化物、硝酸塩、リン酸塩、酢酸塩、水酸化物等の電解質溶液に、アンモニア又はアミン、イミン、イミダゾール等の塩基性窒素を含有する化合物を加えると、金属アンミン錯体が生成する。一般に金属錯体は、配位子を１種以上配位している。アンミン錯体も同様で、アンモニア又はアミン、イミン、イミダゾール等の塩基性窒素を含有する化合物を配位子として１種以上配位している。金属の種類によってそれぞれ最も安定な配位子の数があり、例えば銅錯体の場合は４配位子が安定である。どの様な配位数でも蛋白質繊維類とは化学結合し得るが、金属と最も安定な形になるようなモル比以上の前記の塩基性窒素を含有する化合物を加えると良好な金属アンミン錯体溶液が得られる。この錯体はアルカリ性で安定で水に良く溶け、均一な金属アンミン錯イオン溶液を与える。

【００１１】前記の電解質の濃度は溶解度以下ならいくらでも良く、塩基性窒素を含有する化合物の電解質に対する倍率もいくらでも良いが、好ましくは当該電解質を金属原子として０．５～３０重量%、塩基性窒素を含有する化合物を当該電解質に対して４～１２倍モルを含む水溶液が好適である。当該金属原子が０．５重量%より少なければ担持速度が遅く、３０重量%より多くなると結合しない金属アンミン錯体の量も多くなり、処理後の洗浄の際にロスが多くなる。塩基性窒素を含有する化合物の当該電解質に対する倍率が、最も安定に形成する倍率より低い場合には、当該電解質が全てアンミン錯体にならず、一部水酸化物として沈殿するので、沈殿したものについては十分な担持速度と担持力が得られない。

【００１２】こうして得られた金属アンミン錯体溶液に、繊維状、フィルム状、塊状等のウール、シルク、羽毛等の蛋白質繊維類を浸漬すると、極めて速く金属アンミン錯イオンと蛋白質繊維類とが反応して、金属アンミン錯イオンと蛋白質繊維類とが化学結合した抗菌防臭ならびに消臭性能を有する組成物を与える。この担持は極めて速く起こりしかも金属を強固に担持する。実用的には３０秒程度の浸漬時間で十分である。これを脱液、水洗することにより過剰の金属アンミン錯体を取り除くと、金属を強固に担持した蛋白質繊維類からなる組成物が得られる。水洗後も担持されている金属は蛋白質繊維類と強固な化学結合をしている。



【００１３】蛋白質繊維類に担持させる金属としては、銅、亜鉛、銀が挙げられる。

【００１４】本発明において用いられる蛋白質繊維類としては、ウール、シルク、羽毛等、及びこれらを含有する材料が挙げられる。また形状としては繊維状、フィルム状（織布状、不織布状）、塊状等が挙げられるが、連続生産可能な形状のものが好ましい。

【００１５】本発明の組成物は、上述のとおり、金属アンミン錯体アルカリ溶液に蛋白質繊維類を浸漬することにより得ることができる。この金属アンミン錯体アルカリ溶液を用いることにより蛋白質繊維類に大量の金属を極めて速く担持させることができ、さらに蛋白質繊維類への金属の担持力が強いことから、担持された蛋白質繊維類からの金属アンミン錯体および金属の粉末の脱落による汚れが発生しない。さらに連続生産が可能であり生産速度が極めて速いことから生産性に優れる。

【００１６】また、金属アンミン錯体アルカリ溶液に浸漬する前の蛋白質繊維類（処理前の蛋白質繊維類）を酸またはアルカリ水溶液に浸漬する前処理を施すことによって、前処理を施さないものと比べ、担持速度が速く且つ担持力が強い組成物を得ることもできる。これは蛋白質を酸またはアルカリ水溶液に接触させると、蛋白質のペプチド結合が部分的に加水分解されアミノ基とカルボキシル基が生じるためであり、アミノ基及びカルボキシル基と金属アンミン錯イオンとは容易に化学結合することから、蛋白質繊維類への金属の担持速度及び担持力も向上する。しかし、担持速度及び担持力を向上させるため、アミノ基及びカルボキシル基を生じさせる、つまりペプチド結合を加水分解させると、蛋白質繊維類自体の表面（風合い）や物理的特性（強度）が低下する傾向を示すことから、前処理に用いる処理液は次の範囲で用いることが好ましい。（１）濃度５０重量%以下、好ましくは濃度１～２０重量%の酸水溶液、あるいは（２）濃度５０重量%以下、好ましくは濃度１～２０重量%のアルカリ水溶液.

【００１７】以上のようにして得られた本発明の組成物は、単独あるいは他の素材と合わせ、綿状、糸状、紐状、織物状、紙状、不織布、粉末状、マイクロビーズ状、フィルム状、スポンジ状、ハニカム状、筒状又は塊状など、あらゆる形に加工成形することができる。また本発明の組成物自体は粉末による汚染が極めて少なく、さらに加工時においても粉末による汚染が極めて少ないため、成形品への粉末付着による汚染が極めて少ない利点を有する。

【００１８】

【実施例】以下に実施例をあげて本発明を説明するが、本発明はこれらに限定されるものではない。なお、実施例の組成物の各評価方法は以下による。

【００１９】消臭性能試験

消臭性能試験の装置の概略図を図５に示す。１．５Ｌ容量のファスナーバッグには予め、脱気口、ガス封入口及び検知管差込口としてコック付きコネクターを取り付けておく。ファスナーバッグに測定試料１ｇを入れファスナーを完全に閉め脱気した後、ポンプを用いて１００ｐｐｍの硫化水素を１．５Ｌ封入する。封入終了時間を０分とし、一定時間経過ごとに北川式検知管にてガス濃度を測定する。なお、本実施例の評価における硫化水素は、予め１００ｐｐｍに調製された硫化水素ガスボンベを用いた。

【００２０】洗濯試験

ＪＩＳ　Ｌ－０２１７　１０３法に準じた。

【００２１】抗菌試験

繊維製品衛生加工協議会の定める「抗菌防臭加工製品の加工効果評価試験マニュアル」の菌数測定法に準じた。なお本実施例の評価における試験菌体は、黄色ブドウ状球菌を用いた。

【００２２】実施例１

３重量%の硫酸銅水溶液に、アンモニアが硫酸銅の６倍モルになるように２５重量%濃度のアンモニア水を加え濃紺色の銅アンミン錯体水溶液を得た。これに浴比が３０倍になるように、精製羊毛を室温で３０秒間浸漬し、次いで脱液、水洗、乾燥して、銅を担持した羊毛（組成物１）を得た。得られた組成物１の評価結果は次のとおりであった。硫化水素に対する消臭性能を図１に示す。銅含有量は組成物１中４．０重量%、洗濯試験（１０回）後の含有量は３．９重量%。抗菌試験結果は４．２、洗濯試験（１０回）後の抗菌試験結果は４．０。また組成物１は原料にあたる精製羊毛と比較し、風合いは同程度であり、物理的物性も表１に示すとおり同等の値を示した。

【００２３】

【表１】

| | 精製羊毛 | 組成物１ |
|---|---|---|
| 乾強度　(g／d) | １．４ | １．４ |
| 湿潤強度 (g／d) | １．２ | １．２ |
| 伸度　(％) | ３０ | ３０ |

【００２４】

【図１】

【００２５】実施例２

３重量%の硫酸亜鉛の水溶液に、アンモニアが硫酸亜鉛の６倍モルになるように２５重量%濃度のアンモニア水を加え、無色透明の亜鉛アンミン錯体水溶液を得た。これに浴比が３０倍になるように、羽毛布団用の羽毛を室温で３０秒間浸漬し、次いで脱液、水洗、乾燥して亜鉛を担持した羽毛（組成物２）を得た。得られた組成物２の評価結果は次のとおりであった。硫化水素に対する消臭性能を図２に示す。亜鉛含有量は組成物２中３．８重量%、抗菌試験結果は３．７。この結果より組成物２は十分な抗菌防臭ならびに消臭性能を有することが認められる。

【００２６】

【図２】

【００２７】実施例３

３重量%の塩化銀水溶液に、アンモニアが塩化銀の６倍モルになるように２５重量%濃度のアンモニア水を加えて銀アンミン錯体水溶液を得た。これに浴比が３０倍になるように、絹繊物を室温で３０秒間浸漬し、次いで脱液、水洗、乾燥して銀を担持した絹繊物（組成物３）を得た。得られた組成物３の評価結果は次のとおりであった。硫化水素に対する消臭性能を図３に示す。銀含有量は組成物３中３．９重量%、洗濯試験（１０回）後の含有量は３．８重量%。抗菌試験結果は３．８、洗濯試験（１０回）後の抗菌試験結果は３．６。この結果より組成物３は十分な抗菌防臭ならびに消臭性能を有することが認められる。

【００２８】

【図３】

【００２９】実施例４

実施例１に用いた精製羊毛の代わりに、５重量%硫酸水溶液に浴比が３０倍になるように精製羊毛を室温で１０分間浸漬し、次いで脱液、水洗、乾燥して得た前処理羊毛（活性化羊毛）を用いた以外は、実施例１と同様にして銅を担持した活性化羊毛（組成物４）を得た。得られた組成物４の評価結果は次のとおりであった。硫化水素に対する消臭性能を図４に示す。銅含有量は組成物１中４．８重量%、洗濯試験（１０回）後の含有量は４．７重量%。抗菌試験結果は４．７、洗濯試験（１０回）後の抗菌試験結果は４．６。この結果より組成物４は十分な抗菌防臭ならびに消臭性能を有することが認められる。

【００３０】

【図４】

【００３１】

【発明の効果】本発明の製造方法によれば、該組成物の強度や風合い等の性質を損なうことなく該組成物に大量の金属化合物を担持させることができる。また、極めて速く担持させることができ、また、製造工程や加工工程で金属化合物粉末の脱落による汚れが発生しないため、生産性の優れたものである。また、この様にして、得られた抗菌防臭ならびに消臭性組成物は、組成物本来の強度や風合い等の性質は損なわれておらず、アンモニア、トリメチルアミン等のアルキルアミン、硫化水素、メチ

ルメルカプタン類等の硫黄化合物、ホルマリンなどの悪臭物質と反応して著しい消臭性能を発揮する。一方、金属原子の持つ抗菌作用により、黄色ブドウ状球菌等に対し強い抗菌性を示す。また、金属化合物は組成物に強固に担持されているため、洗濯耐久性等に優れたものである。

【図面の簡単な説明】

【図１】実施例１において得られた組成物１の洗濯前及び洗濯１０回後の硫化水素に対する消臭性能を示す。

【図２】実施例２において得られた組成物２の硫化水素に対する消臭性能を示す。

＊【図３】実施例３において得られた組成物３の洗濯前及び洗濯１０回後の硫化水素に対する消臭性能を示す。

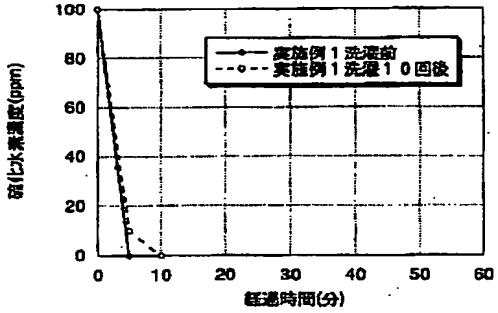
【図４】実施例４において得られた組成物４の洗濯前及び洗濯１０回後の硫化水素に対する消臭性能を示す。

【図５】消臭性能試験の装置の概略図を示す。

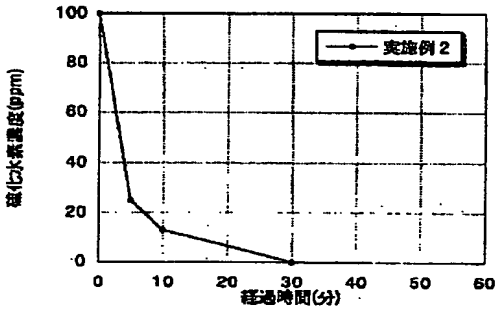
【符号の説明】

1　ファスナーバッグ
2　コック付きコネクター
3　シリコンチューブ
4　検知管
5　サンプリングポンプ

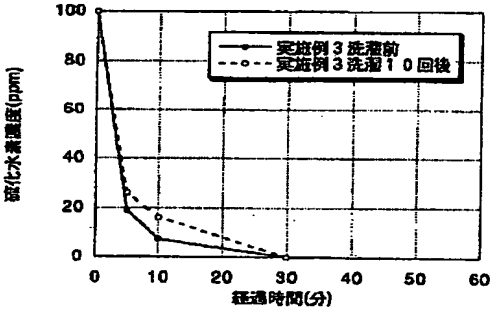
【図１】



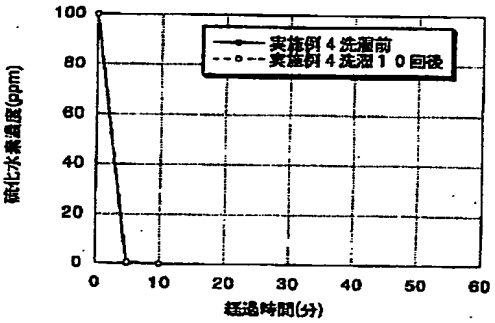

【図２】




【図３】




【図４】




【図５】